TECHNICAL GUIDANCE MANUAL

Contaminant Flux Reduction Barriers for Managing Difficult-to-Treat Source Zones in Unconsolidated Media

ESTCP Project ER-201328

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14. ABSTRACT
The overall objective of this project was to evaluate if inexpensive flow reduction agents delivered via permeation grouting technology could help manage difficult-to-treat chlorinated solvent source zones. This approach aims to provide two benefits for improving groundwater quality at chlorinated volatile organic carbon (CVOC) sites by: 1. physically reducing the mass flux of contaminants leaving the source zone by using permeation grouting, thereby reducing risk and making the downgradient plume more amenable for management by natural attenuation processes; and 2) increasing the Natural Source Zone Depletion (NSZD) rate within the source by diverting competing electron acceptors around the source zone to create an enhanced reductive dechlorination zone (ERDZ). This report describes the results of a Small-Scale Demonstration that achieved an average 64% reduction in flow through three small barriers. This was lower than the performance objective of a 90% reduction in flow and was likely caused by the low permeability of the silty sands in the test area. Finally, applications of one acre in area or more are significantly less costly than conventional in-situ remediation technologies ($996K per acre and $21 per cubic yard for a one acre site).

15. SUBJECT TERMS
Barrier, ERDZ, NSZD, Chlorinated Solvents, Grouting

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ACRONYMS AND ABBREVIATIONS

bgs	Below Ground Surface
cm/sec	Centimeter per Second
cP	Centipoise
CVOC	Chlorinated Volatile Organic Carbon
DBE	Dibasic Ester
DNAPL	Dense Non-Aqueous Phase Liquid
DoD	Department of Defense
ERDZ	Enhanced Reductive Dechlorination Zone
ESTCP	Environmental Security Technology Certification Program
EVO	Emulsified Vegetable Oil
ft	Foot, Feet
gal	Gallons
gpm	Gallons per Minute
H_2O	Water
HASP	Health and Safety Plan
in	Inch
kg	Kilogram
m	Meters
MNA	Monitored Natural Attenuation
NaSi	Sodium Silicate
NSZD	Natural Source Zone Depletion
PFM	Passive Flux Meter
psi	Pounds Per Square Inch
PVC	Polyvinyl Chloride
Vol-%	Percentage by Volume
Wt-%	Percentage by Weight
yd^3	Cubic Yard

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EXECUTIVE SUMMARY

Project Objective

The overall objective of this project was to evaluate if inexpensive flow reduction agents delivered via permeation grouting technology could help manage difficult-to-treat chlorinated solvent source zones. This approach aims to provide two benefits for improving groundwater quality at chlorinated volatile organic carbon (CVOC) sites by:

1. physically reducing the mass flux of contaminants leaving the source zone by using permeation grouting (Figure 1), thereby reducing risk and making the downgradient plume more amenable for management by natural attenuation processes; and

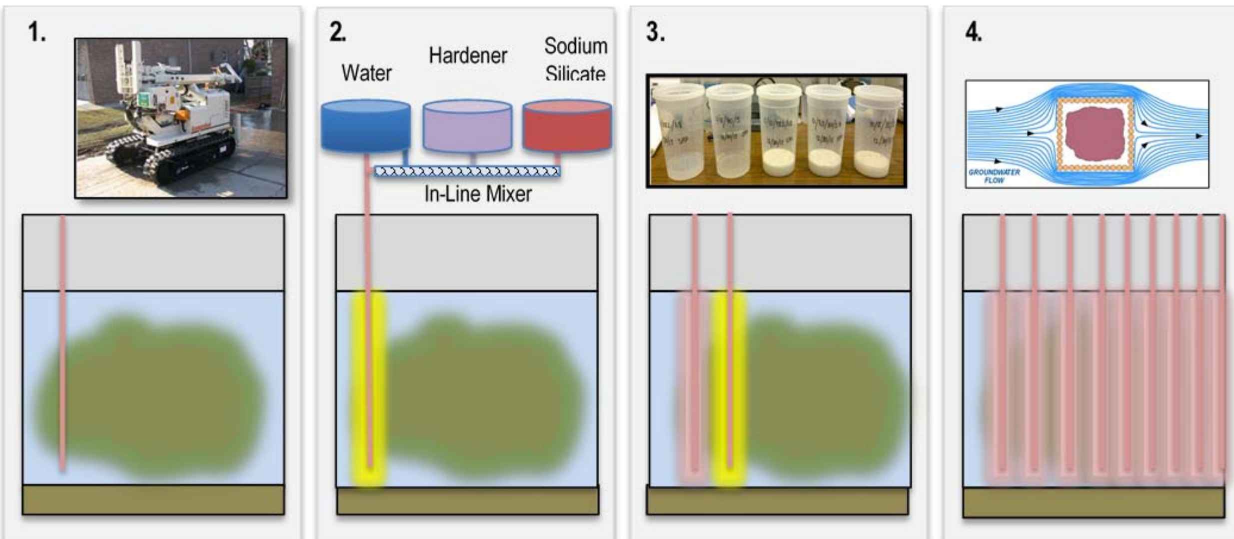

Figure 1. Permeation Grouting Sequence

(1) A small injection point (either inexpensive single use multi-level well or direct push injection point that injects while pulling up) is driven into source zone. (2) Water, hardener, and silica gel are mixed on the surface and injected as a liquid into the injection point, filling up the pore space of the sands. (3) After 0.5 to 4 hours, the silica gel changes from liquid state to a gel state, greatly reducing the water flow through the sand/gel mix. (4) The process is repeated by drilling and injecting in adjacent injection points (spaced 0.8–2 m apart), forming a barrier around the source.

2. increasing the Natural Source Zone Depletion (NSZD) rate within the source by diverting competing electron acceptors (e.g., dissolved oxygen, nitrate, and sulfate) around the source zone to create an enhanced reductive dechlorination zone (ERDZ) (Figure 2).

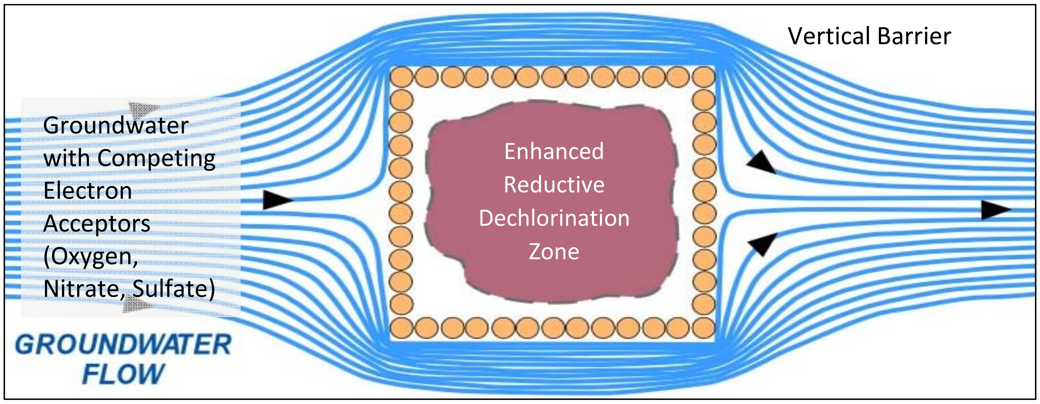

Figure 2. Enhanced Reductive Dechlorination Zone Concept

Electron acceptors that flow into a CVOC source zone can consume valuable electron donor. Diverting them can increase the NSZD rate.

1.0 WHY BUILD A BARRIER?

There are two reasons to build a contaminant flux barrier around a chlorinated solvent source zone:

1. You can physically reduce the mass flux of contaminants leaving the source zone, thereby reducing risk and making the downgradient plume more amenable for management by natural attenuation processes; and
2. You can increase the NSZD rate within the source by diverting competing electron acceptors (e.g., dissolved oxygen, nitrate, and sulfate) around the source zone to create an enhanced reductive dechlorination zone (ERDZ). The influx of competing electron acceptors into treatment zones can consume a large fraction of the available electron donor supply at bioremediation sites, necessitating more frequent substrate reinjection. One research paper (Newell and Aziz, 2004) estimate a potential increase in NSZD rates of 226 kilogram (kg)/year (500 lbs/yr) at a typical chlorinated solvent site with electron acceptor diversion and 100% efficiency; see Appendix A for an example calculation at a hypothetical site and the BIOBALANCE tool (Kamath et al, 2008) for more information.

Natural Source Zone Depletion (NSZD) and Enhanced Reductive Dechlorination Zones (ERDZs)

NSZD is the term for the attenuation of the source zone itself at a contaminated groundwater site from processes such as mass loss to moving groundwater and biodegradation in the source zone (Newell et al., 2014)

One way to increase NSZD rates at chlorinated solvent sites is to use a barrier to divert competing electron acceptors (oxygen, nitrate, and sulfate) around the source zone, thereby making the geochemistry inside the barrier more conducive for anaerobic biodegradation. This is called an ERDZ (Kamath et al., 2008)

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2.0 WHAT ARE THE SITE REQUIREMENTS?

To use conventional barrier construction techniques to reduce the mass flux leaving the source zone, the site must be:

- Comprised of unconsolidated material (gravel, sand, silt, clay)
- Have access around the source zone to building the barrier
- Not have a near term requirement to restore groundwater
- For high efficiency barriers with significant flow reduction, the site must have a lower low permeability unit such as a clay to prevent up flow
- For accessing the lower cost silica gel grouting technology, the hydraulic conductivity of the transmissive unit should be in the range of $5x10^{-4}$–10^{-2} centimeter per second (cm/sec).

To obtain the benefits of an ERDZ, a key requirement is that the site is contains electron donor in the source zone, either that is from naturally occurring organic material in the source zone; fermentable oils or other electron donors that were released along with the chlorinated solvents (a fairly common occurrence at Department of Defense [DoD] sites); or there has been an election donor addition project to accompany the construction of the barrier.

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3.0 WHAT ARE THE OPTIONS FOR BUILDING A BARRIER?

Figure 3 presents the decision logic for applying contaminant mass flux barriers.

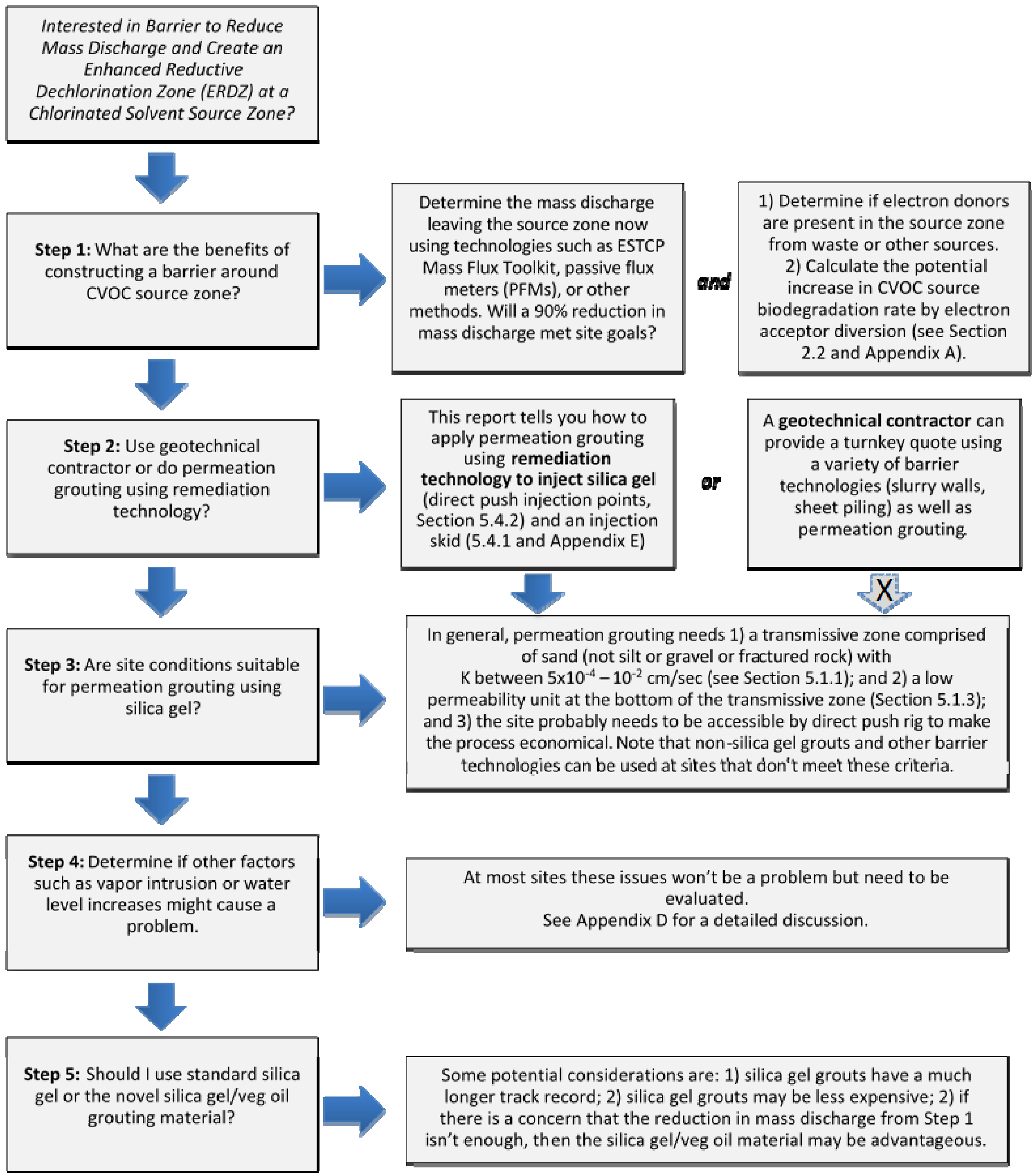

Figure 3. Decision Logic for Applying Barrier Technology at CVOC Sites

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4.0 WHAT WERE THE LESSONS LEARNED FROM THIS ESTCP PROJECT?

4.1 USING EXISTING REMEDIATION TECHNOLOGY FOR BARRIERS

- This Environmental Security Technology Certification Program (ESTCP) demonstration was able to use existing remediation technology (direct push rigs and injection skids) to build four small barriers for the Small-Scale Demonstration.

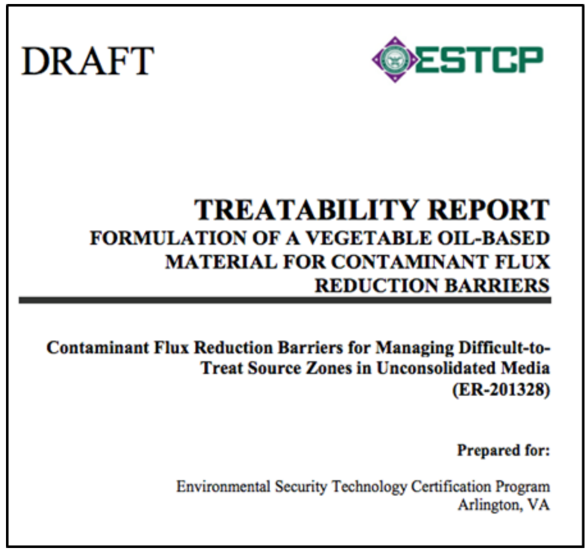
- The mixing process is generally more complex than standard injection-based remediation projects because the injection skid needs to mix three fluids, delivery multiple locations simultaneously, let operators see pressure, flowrate, and have contingency for grout set-up in the injection manifolds. The design described in Section 5.4 and Appendix E worked well.

4.2 DESIGNING PERMEATION GROUT BARRIERS

- Permeation grouting requires filling all the porosity, not just the mobile porosity (see Payne et al. 2008 for a discussion of the mobile porosity concept). This increases the amount of grout required for the barrier as total porosity in the 24%–44% range are typically used for the volume of grout needed calculation compared to 2%–10% for the mobile porosity. Note the Small-Scale Demonstration and the calculations in Section 6 assumed 30% porosity for the fine sand present in the test area.
- Munitions can complicate installation, but same holds for any injection based technology.
- The silica gel grout was much more reliable in terms of grouting times when the inorganic hardener (dibasic ester [DBE]) was used (Section 5.3). On-site gel tests are important to confirm that the soil chemistry will work with the design mix of gel and hardener (Section 6.1.2). This is particularly true at sites with saline groundwater.
- If a direct push rig is used for injection and the injection zone is more than a few feet (ft) thick, multi-level injection wells (Section 5.4.2) are important to ensure even vertical distribution of the grout. If a permeation grouting contractor is used, a tube-a-manchette rig will provide good vertical distribution of grout in the barrier.

4.3 NOVEL GROUTING MATERIAL

- The Solutions-IES novel grout material consisting of a silica gel/veg oil mix appeared to work as well as conventional silica gel for reducing flow, but since the Small-Scale Demonstration was performed in a relatively unimpacted zone, the project was unable to test its dechlorination capabilities in the field. The theory behind the gel/oil material is sound as permeation grouting barriers are designed to reduce but not eliminate groundwater flow through them, therefore providing a mechanism for increased treatment with the oil.



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ESTCP

TREATABILITY REPORT
FORMULATION OF A VEGETABLE OIL-BASED MATERIAL FOR CONTAMINANT FLUX REDUCTION BARRIERS

Contaminant Flux Reduction Barriers for Managing Difficult-to-Treat Source Zones in Unconsolidated Media (ER-201328)

Prepared for:

Environmental Security Technology Certification Program
Arlington, VA

5.0 WHAT ARE THE ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

5.1 ADVANTAGES

The key advantage of this technology is that creating flow/mass flux reduction barriers around the perimeter of difficult-to-treat source zones is less expensive than treating the entire volume of the source zone. In addition, there are potential benefits of reducing the influx of competing electron acceptors, thereby establishing an Enhanced Reduction Dechlorination Zone at chlorinated solvent sites that already contain electron donors within the source zone.

Costing models show that this technology has the potential to be significantly cheaper (approximately $21 per cubic yard for large sites; see Figure 4) provide better performance, and be more predictable and reliable than existing technologies for larger sites. Unlike most remediation systems in which costs are directly proportional to the size of treatment areas, this technology has decreasing costs per source zone area. If proven to be feasible, the proposed methods are also easy to implement and scale up, making them attractive options for closing large sites. See Section 9 and Kulkarni et al. (2017b) for more information about costs.

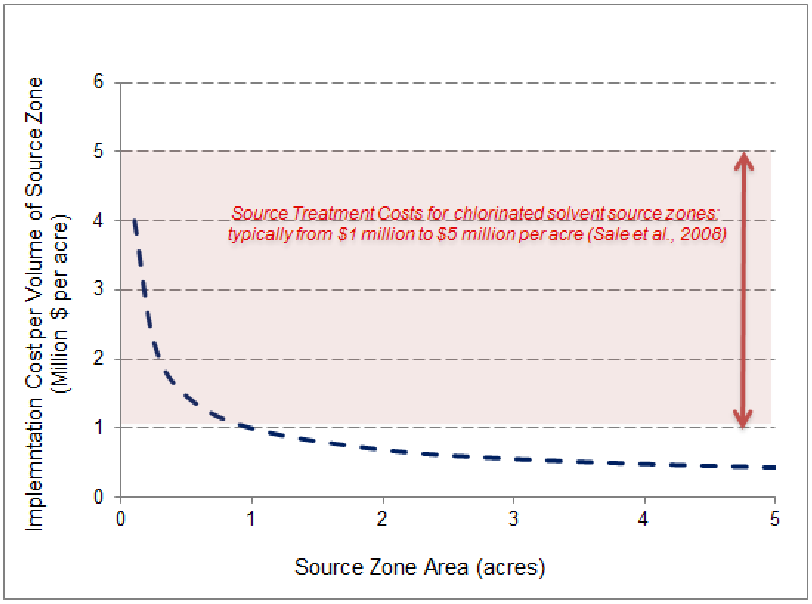

Figure 4. Approximate Cost Model for Application to Various Source Zone Areas

Additionally, little to no maintenance and operating costs are involved, making this a very cost-effective technology over the long-term. The lifetime of most grouts is relatively long; for example cement grouts are expected last indefinitely unless in unusual groundwater conditions. One grouting reference (Karol, 2003) stated that silica gel grouts are expected to have a 50-year lifetime. The implementation of this technology also requires minimal subsurface disturbance and waste materials.

Finally, the technology provides an isolation of the source zone or plume, reduces mass discharge, and enhances biodegradation within the treatment zone.

5.2 LIMITATIONS OF THE TECHNOLOGY

Potential limitations of the technology include:

- No direct active treatment and reliance on NSZD alone for treatment may not be acceptable to site stakeholders. Even though the NSZD rate of the chlorinated solvents in the source zone is likely to be increased, longer remediation timeframes are expected compared to active treatment.
- The silica gel / injected materials are semi-permanent, making complete restoration of the treatment zone to pre-impact conditions difficult;
- The technology does not control the vapor intrusion pathway, and other controls will be required if this pathway is active;
- At a small number of sites, the accumulation of water within the barriers and elevated water levels may occur if the barrier is too tight and does not have a method to release accumulated groundwater.
- Access may be a problem for construction of the barrier, but this is likely to be a much smaller problem compared to application of most in-situ treatment technologies.
- High mobilization costs may make the technology less cost-effective for small sites.

6.0 WHAT ARE THE TECHNICAL AND REGULATORY DRIVERS FOR FLUX REDUCTION BARRIERS?

6.1 TECHNICAL DRIVERS

SERDP/ESTCP recently identified *"Treatment of Contaminants in Low-K Zones"* as a "High" Research and Development need for the DoD remediation program (Leeson and Stroo, 2011). These types of sites represent an increasing fraction of the DoD's chlorinated site portfolio, as the easier and smaller source zones are successfully treated. For example, sites dominated by matrix diffusion-type sources from low permeability (low-K) zones are increasing for two reasons: (1) untreated sites continue to age and transform from Middle Stage sites (sites where Dense Non-Aqueous Phase Liquid [DNAPL] sources are active) to Late Stage Sites (sites where matrix diffusion sources dominate) (Sale et al., 2008); and (2) more chlorinated solvent sources zones are treated and the bulk of the DNAPL is removed, but the low-permeability source zones are still too strong to close the site or rely on Monitored Natural Attenuation (MNA) processes.

One of the likely side effects of matrix diffusion dominated sites is concentration rebound after in-situ treatment. This has been commonly observed at sites treated with chemical oxidation (e.g., McGuire et al, 2005; Krembs et al., 2010), and it has been speculated that rebound can occur at sites treated with in situ bioremediation if monitoring is continued for longer periods. A key paper describing sustained treatment (Adamson et al., 2011) makes the case that even for apparent long-lasting technologies, some of the treatment effects will diminish over time, and that periodic reapplication of treatment chemicals may be needed over the lifetime of the site. If this is the case, then the DoD's remediation liability over the decades-long periods that these sources will be active may be much larger than currently estimated.

For these long-lived, difficult-to-treat sites, inexpensive (in units of dollars per cubic yard, or dollars per acre) technologies are needed that can: (1) immediately and reliably address the key problem associated with these recalcitrant source zones, specifically the mass flux of contaminants leaving the source zone; (2) increase the actual treatment of the contaminants leaving low-K source zones, or DNAPL; and (3) last for decades or longer. To evaluate the impact of remediation at these sites, mass flux (or mass discharge) is the most useful measurement because it establishes the amount of mass per unit time leaving the source zone (Newell et al., 2011).

The project envisions site managers could access the technology in two ways:

1. Contract existing geotechnical permeation grouting vendors to install physical barriers at contaminated sites, either using permeation grouting or other barrier techniques (e.g., slurry walls, sheet piling). This has the advantage of simpler turn-key approach, but may have the disadvantage of higher costs if the contractor is unfamiliar with and untrained for working at hazardous waste sites. Note that permeation contractors have a specialized tool called tube-a-manchette that they use for many permeation grouting projects.
2. Use existing remediation contractors for applying direct push technology and modified injection skids to perform the permeation grouting. Most of the project was devoted to explaining how to perform permeation grouting can be implemented by using conventional remediation technology.

Contaminant flux reduction barriers can potentially prove to be an innovative application of existing technologies that can meet these objectives inexpensively and reliably. This technology provides long-term (decades) or permanent treatment of source zones where the mass flux is greatly reduced, back diffusion and DNAPL sources are reliably managed, and contaminant attenuation rates within the source zone are substantially increased. Unit costs for flux reduction treatment of an acre site are anticipated to be ~ $21 per cubic yard and < $1 million per acre. This is significantly less than reported unit cost for in-situ biodegradation ($30-180 per cubic yard), chemical oxidation (median $125 per cubic yard), and thermal remediation (median $161 per cubic yard) (McGuire et al., 2016); and lower than the analysis presented in Sale et al. (2008) that showed that costs for chlorinated solvent source zone remediation "will range between $1 million and $5 million per acre." For the performance criteria for this project, it was assumed a typical in-situ remediation cost of $**3 million per acre.**

6.2 REGULATORY DRIVERS

SERDP/ESTCP recently identified *"Treatment of Contaminants in Low-K Zones"* as a "High" Research and Development need for the DoD remediation program (Leeson and Stroo, 2011). These types of sites represent an increasing fraction of the DoD's chlorinated site portfolio, as the easier and smaller source zones are successfully treated. For example, sites dominated by matrix diffusion-type sources from low permeability (low-K) zones are increasing for two reasons: 1) untreated sites continue to age and transform from Middle Stage sites (sites where DNAPL sources are active) to Late Stage Sites (sites where matrix diffusion sources dominate) (Sale et al., 2008); and 2) more chlorinated solvent sources zones are treated and the bulk of the DNAPL is removed, but the low-permeability source zones are still too strong to close the site or rely on MNA processes.

The National Research Council (NRC) has recently advanced an important new concept about managing contaminated groundwater sites called a Transition Assessment. Despite years of effort and considerable investment, many sites "will require long-term management that could extend for decades or longer." The NRC discusses the need for developments that can aid in "transition from active remediation to more passive strategies and provide more cost-effective and protective long-term management of complex sites," including conducting formal Transition Assessments. This concept, which is an intrinsic part of the ITRC's Integrated DNAPL Site Strategy (IDSS) framework, has now been validated by a key U.S. scientific body, the National Research Council.

The Contaminant Flux Reduction Barrier technology is targeted to address sites dominated by matrix diffusion and that are candidates for long-term passive management of a site. At these sites, further active remediation (such as chemical oxidation, bioremediation, chemical reduction, thermal treatment) will likely not change the long-term management of the site because of the residual contaminants in low permeability zones. If MNA will not be protective, there is a need for a technology that will reduce the mass flux from these zones and have the potential for some accelerated NSZD of the remaining chlorinated solvent mass.

7.0 WHAT ARE SOME KEY DESIGN CONSIDERATIONS FOR CONSTRUCTION?

7.1 DESIGN RESOURCES FOR PERMEATION GROUTING

Two key design references for permeation grouting are Powers et al. (2007) and Karol et al. (2003)

- Karol, Reuben H., 2003. *Chemical Grouting and Soil Stabilization,* 3d ed., Marcel Dekker, Inc., New York, New York.
- Powers, J. Patrick, Arthur B. Corwin, Paul C. Schmall, and Walter E. Keck, 2007. *Construction Dewatering and Groundwater Control: New Methods and Applications,* 3d ed., John Wiley & Sons, Inc., Hoboken, New Jersey.

GSI performed a detailed literature review of conventional permeation grouting techniques. The most useful design reference is Powers et al., 2007 (Chapter 22). Note there are some conflicting guidelines for applicability of permeation grouting, such as the minimum hydraulic conductivity specified in the data shown in Table 1 and the silica gel "rule of thumb" below. Key figures, tables, and information include:

- Applicability of various grout materials vs. hydraulic conductivity (Powers Figure 22.6, summarized in Table 1 of this report below). Concrete grouts are more commonly used for coarse alluvial material; silica gel grouts are applied to fine alluvial material (gravels and sands; sands; and silty sands).
- Grain size vs. percent passing chart to indicate groutability (Powers Figure 22.7).
- Chemical groutablity chart vs. percent passing through 200 sieve: < 12%: Good; 12-20%: Moderate; 20-25%: Marginal; > 25%: Poor.
- Usual Range of Pre-Grouting and Post-Ground Hydraulic Conductivity (Figure 22-9). Generally the cleaner and coarser the ground, the greater (in orders of magnitude) the potential reduction in hydraulic conductivity. Note it has a higher minimum hydraulic conductivity for permeation grouting with silica gel grout: 10^{-2} cm/sec.
- *"The generally accepted rule of thumb, based on history, is that one to two orders of magnitude of hydraulic conductivity reduction is possible and 1 X 10^{-5} cm/ sec is the lowest practically achievable hydraulic conductivity with sodium silicate grout." (page 4-20).*
- Viscosities of typical grouts (Powers Figure 22.10)
- Typical properties of Sodium Silicate (NaSi) (Powers Table 22.3)
- Grout characteristics: Liquid State vs. Hardened State (Powers Table 22.3)
- NaSi Viscosity Relative To Water At Various Concentrations (Powers Table 22.4)
- Range of Typical Permeating Grout Pipe Spacing in Soil: Fine Sand: 2.6 to 4.3 ft; Sand, sand and gravel: 3.3 to 6.6 ft; Gravel: 6.6 to 13.2 ft
- Viscosity vs. time behavior of a NaSi grout (Powers Figure 22.12)
- Setting time of NaSi grout with di-ester hardener (Powers Figure 22.13)

- Gallons (gal) of grout per vertical ft vs. radius of grout spread (Powers Figure 22.32)
- NaSi’s are the most commonly used grouts.
  - Acrylates are recent substitutes for acrylamide grouts where toxicity concerns resulted in a sharp decline in application in the 1970s. Acrylate grouts have very low viscosity (2-3 centipoise [cP]) but require the mixing of up to five different compounds, making application more complicated.

Table 1. Applicability of Various Water Tightening Grouts vs. Hydraulic Conductivity (Powers et al., 2007)

(Silica Gel Bolded)

	Range of Application Hydraulic Conductivity (cm/sec)	Notes
Clay-cements	$1x10^{-1} – 1x10^{2}$	
Silica Gel (Concentrated)	$\mathbf{5x10^{-4} – 5x10^{-2}}$	*Lower range may be limited by cost*
Silica Gel (Low Viscosity)	$\mathbf{1x10^{-4} – 1x10^{-2}}$	
Acrylate Grouts / Acrylic Resins	$1x10^{-5} – 1x10^{-3}$	

The next most important reference is Karol (2003) which has a number of photos, design charts, and results of key grouting research from this period. This reference states that silica gel grouts are expected to have a 50-year lifetime. Berry (2000) provides good rules of thumbs and design charts about the design porosity for grouting; this reference indicates that most sands in the saturated zone will have a “wet-packed” porosity between 24% and 44%.

In addition, the Final Report for this ESTCP project provides more detail about the actual field demonstration that was performed.

Kulkarni, P., E. Higgins, B. Strasters, and C. Newell, 2017. Final Report for Contaminant Flux Reduction Barriers for Managing Difficult-to-Treat Source Zones in Unconsolidated Media, ESTCP Project ER-201328. Environmental Security and Technology Certification Program, Arlington, Virginia.

< https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201328/ER-201328 >

7.2 BARRIER CONFIGURATION

Figure 5 shows a conceptual figure of the contaminant flux reduction barrier, showing groundwater flow carrying competing electron acceptors will be diverted from the treatment area, creating an anaerobic, enhanced biodegradation treatment zone. One design consideration is if a square rectangular barrier is needed, or if three-sided barriers are sufficient.

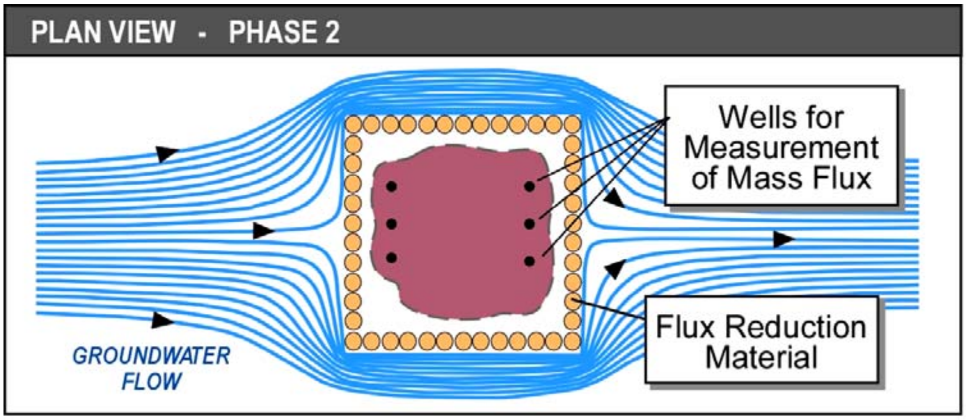

Figure 5. Large-Scale Field Demonstration, Plan View

To answer this question, a limited groundwater flow modeling study of the performance of different barrier configurations was performed using MODFLOW. The model runs assumed:

- Hydraulic conductivity of the formation: $1x10^{-2}$ cm/sec
- Hydraulic conductivity of the barrier wall itself ($1x10^{-5}$ cm/sec) (a conservative value; see right hand column of Table 1)
- Wall thickness: ~3 ft
- Hydraulic Gradient: 0.006 ft/ft

The base case, a four-sided barrier, was predicted to achieve a 97% reduction in groundwater flow through the barrier based on counting the groundwater streamlines (Figure 6a top panel). Three-sided barriers showed a significant reduction in performance: a barrier aligned with groundwater flow with the opening facing downgradient showed only an 80% flow reduction (Figure 6a, bottom panel). A side-open barrier and diagonal barrier showed similar performance as the downgradient barrier: 83% and 74% respectively although there was some subjectivity in which streamlines to count (Figure 6b). Overall the modeling study suggested that four-sided barriers are likely required for good flow reduction, and three-sided barriers are much less effective.

Site experience also indicates that "hanging walls" (barriers that are not keyed into a low permeability zone on the bottom), will have much poorer performance than walls that do have a low permeability bottom.

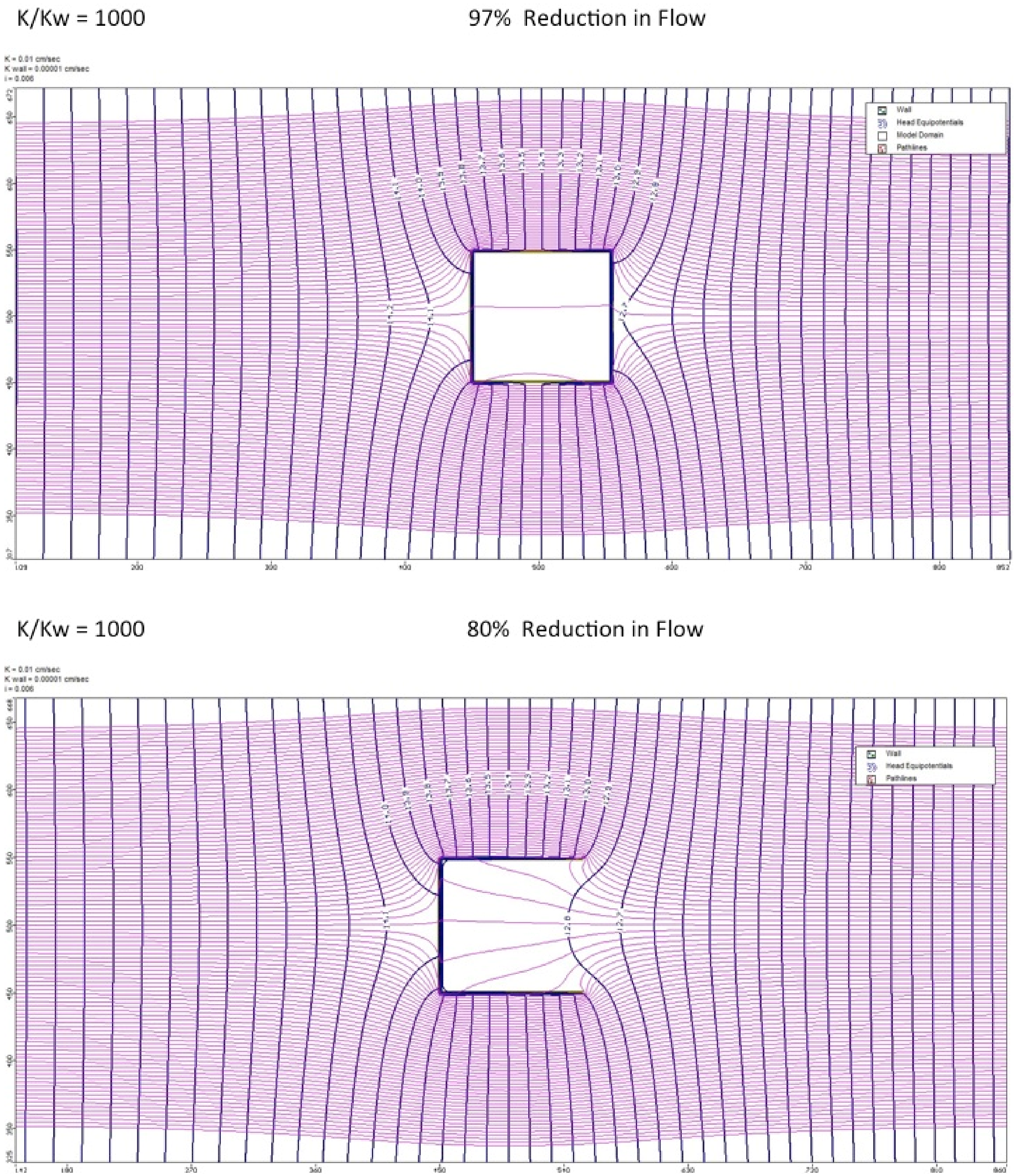

Figure 6a. MODFLOW Groundwater Flow Modeling Showing Streamlines Around 4-Sided Barrier (Top Panel) And Three-Side Barrier With Opening Facing Downstream (Bottom Panel) and Percent Flow Reduction Through Interior of Barrier.

Model Assumptions: K formation: $1x10^{-2}$ cm/sec; K wall itself ($1x10^{-5}$ cm/sec); Hydraulic Gradient: 0.006 ft/ft.

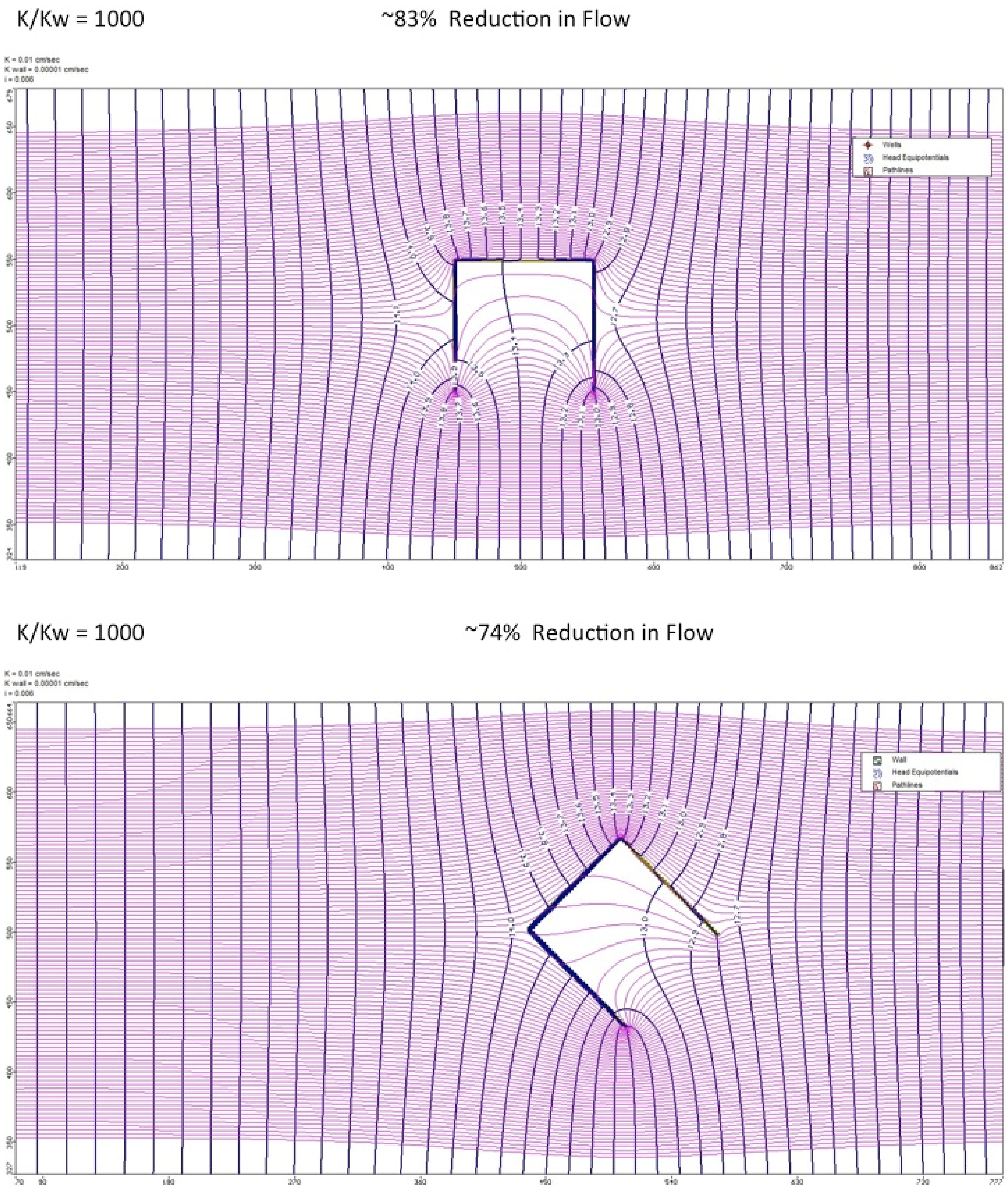

Figure 6b. MODFLOW Groundwater Flow Modeling Showing Streamlines Around 4-Sided Barrier (Top Panel) And Three-Side Barrier With Opening Facing Downstream (Bottom Panel) and Percent Flow Reduction Through Interior of Barrier.

Model Assumptions: K formation: 1x10^{-2} cm/sec; K wall itself (1x10^{-5} cm/sec); Hydraulic Gradient: 0.006 ft/ft.

7.3 PERMEATION GROUTING INJECTION SKID

A skid-based delivery system was designed and was constructed to inject chemical grout to the subsurface. The skid included pumps, tanks, mixers, controls, and piping to facilitate mixing of the selected grout components prior to injection into the subsurface via injection points. The Injection Skid Design Manual is provided in Appendix E for the Final Report (Kulkarni et al., 2017).

7.3.1 Design Requirements

The skid was designed to address the overall objective of the system and to accommodate the following design basis parameters, assumptions, and limitations:

- ***Injection Pressures:*** The skid was designed to deliver chemical grout at injection pressures ranging from 3.8 to 38 pounds per square inch psi, corresponding to 8.7–87 ft of water (H_2O) (Table 2). Typical maximum injection pressures for chemical grouting are set at approximately 1 psi/ft of overburden (Karol, 2003). For some waste injection applications, regulatory authorities may limit the injection pressure to 25% of this amount (RRC, 2014). However, given that some consider the 1 psi/ft of overburden to be overly conservative (Powers et al, 2007); a range bracketing the 1 psi/ft of overburden has been selected as a preliminary design criterion. Therefore, to provide flexibility for testing in the field, the skid was capable of delivering grout under a range of 75% to 125% of the overburden pressure. For the anticipated injection depths of 5 to 30 ft below ground surface (bgs), estimated grout delivery pressures were as follows:

Table 2. Determination of Injection Pressures

Maximum Injection Pressure Recommended	Injection Depth	Injection Pressure	
75% psi/ft of overburden	5 ft	3.8 psi	8.7 ft H_2O
	30 ft	22.5 psi	52 ft H_2O
125% psi/ft of overburden	5 ft	6.2 psi	14 ft H_2O
	30 ft	38 psi	87 ft H_2O

- ***Injection Configuration:*** To ensure efficient and cost-effective barrier construction, grout mixture was injected simultaneously via a manifold into a maximum of 12 locations and depths (i.e., 3 injection points with 4 depth levels per injection point). The 12-branch manifold had the operational flexibility to conveniently change or terminate injection at any individual location and depth while continuing injection at other individual locations and depths.
- ***Injection Flow rates:*** The skid was capable of delivering a total of 1–15 gallons per minute (gpm) of grout, corresponding to 0.1–1.2 gpm per individual location and depth. Actual delivery rates depended on the rate of the subsurface formation to accept the grout.

- ***Grout Mixtures:*** The skid was capable of pumping, mixing, and injecting the grout mixtures currently under consideration, including NaSi with or without emulsified vegetable oil (EVO) and DBE.
- ***Skid Operation:*** The skid was manually operated and controlled. The measurements obtained from any instruments (e.g., pressure gauges, flow indicators) were directly read from the instrument. Piping and valves were configured and labeled to facilitate understanding of how the flow is being routed at any time (e.g., from water supply to dilution tank, from dilution tanks to manifold).

7.3.2 Description and Process Flow through Major Skid Components

A simplified process flow diagram (PFD) for the overall injection system is shown in Figure 7. Each component is described in additional detail below:

- ***Water:*** Clean potable water was obtained from an off-site company and delivered to the site in a poly-tank.
- ***Grout Component Preparation:*** In order to prepare the grout components for injection, concentrated NaSi (with or without EVO) and DBE were transferred from the drums or totes delivered to the site (i.e., Tanks T-01 and T-03, respectively) for dilution in two larger tanks (i.e., Tanks T-02 and T-04, respectively). Dilute NaSi (with or without EVO) was prepared by filling Tank T-02 with a sufficient volume of water and NaSi (with or without EVO) to attain the specified dilution. Dilute DBE was prepared by filling Tank T-04 with a sufficient volume of water and hardener to attain the specified dilution. Concentrated grout components were pumped to the tanks by means of centrifugal pumps (P-02 and P-03).
- ***Tanks for Grout Components:*** Tanks T-02 and T-04 were used for mixing each component with water to create a dilute mixture. These tanks were approximately 750 gal capacity.
- ***Mixing of Grout Components:*** In addition to being used to transfer the as-received grout components to the dilute tanks, Pumps P-02 and P-03 were also used to recirculate dilute tank contents in order to promote mixing, and deliver the dilute grout components to a 6-element, 0.75-inch (in) diameter static mixer. Shut-off valves were opened and closed as required to route the grout components to tanks or the static mixer as required for the particular stage of the preparation or injection process.

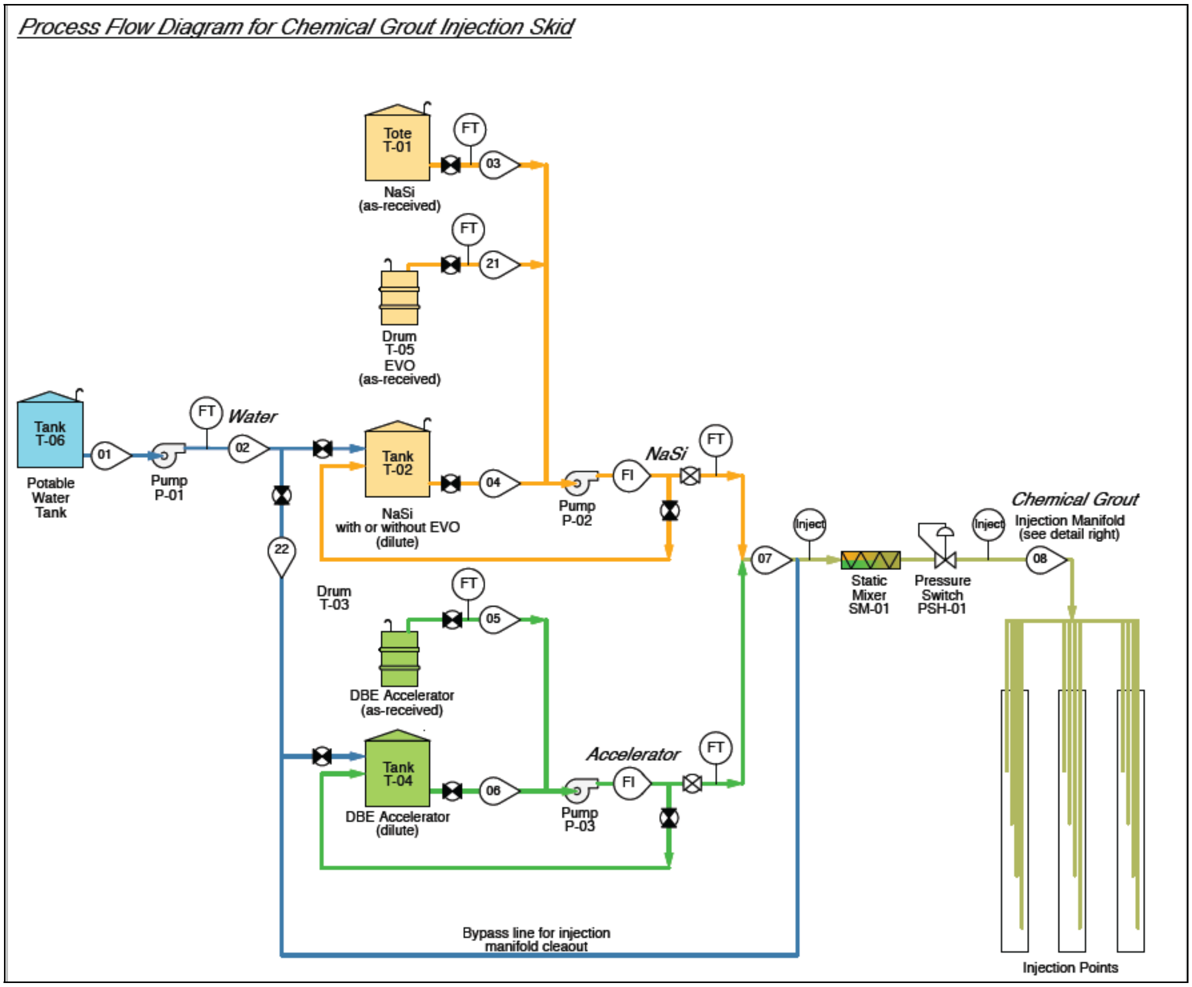

Figure 7. Process Flow Diagram for Chemical Grout Injection Skid

- ***Pressure Regulation:*** A pressure switch (PSH-01) was used to regulate the pressure downstream of the static mixer to ensure a constant pressure to the injection manifold. The injection skid was designed to shut off if the maximum pressure is met or exceeded. This pressure threshold was adjustable in the field.
- ***Injection Manifold:*** A manifold for delivery of the grout mixture to the injection points is described in additional detail below.

7.3.3 Description and Process Flow through Injection Manifold

Details of the injection manifold are depicted on the PFD shown on Figures 8 and 9. As noted above, the grout mixture flowed under constant pressure to the manifold, then into 12 branches of the manifold, and then to the injection points. The manifold and branches were constructed of polyvinyl chloride (PVC), and the individual lines were constructed of 0.5-in diameter, clear, flexible tubing. Each branch was equipped with a pinch valve, an injection point for water, a pressure gauge, flow totalizer, and a sight flow indicator. Flow rate of the grout in each branch was measured quantitatively using a flow totalizer which was placed on the outside of the piping and moved from branch to branch of the manifold.

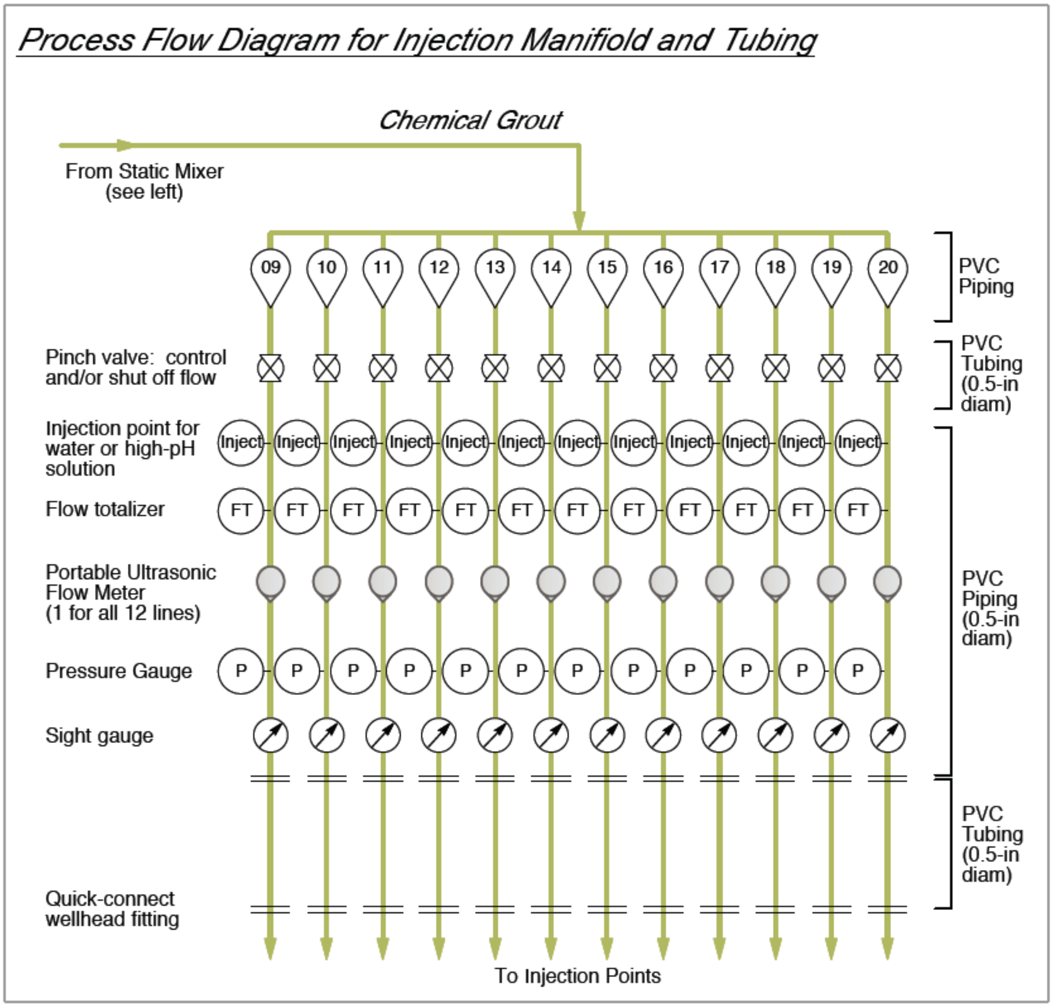

Figure 8. **Process Flow Diagram for Injection Manifold and Tubing**

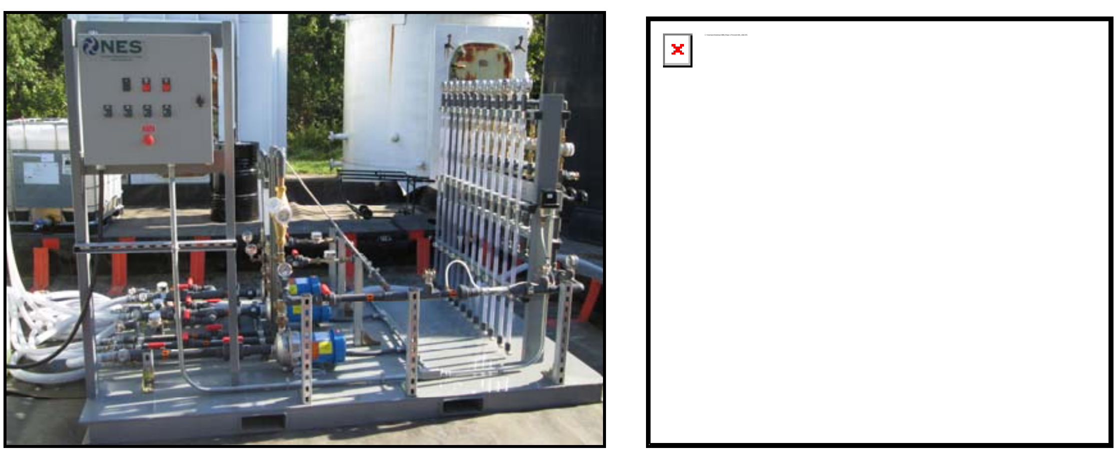

Figure 9. **Injection Skid (Left) and Injection Manifold (Right)**

7.3.4 Measures to Address Potential Clogging of Manifold and Tubing

Clogging could potentially occur within the static mixer, manifold, branches, and tubing downstream of the tee where the NaSi (with or without EVO) and accelerator come together if the residence time within the piping exceeds the planned set time of 3-4 hours. The following design considerations were implemented to deal with potential clogging:

- ***Minimize Number of Parts Subject to Clogging:*** The grout was mixed at the furthest downstream portion of the skid feasible. In addition, flow rates in the individual branches of the manifold were measured using a totalizer, as well as a meter which does not contact the grout.
- ***Use Inexpensive, Replaceable Parts:*** The static mixer, manifold, branches, and injection lines were constructed of inexpensive PVC pipe and tubing which can be replaced if clogged.
- ***Keep Grout Moving:*** In addition to the quantitative flow rates measured by the totalizers, sight flow indicators provided an immediate and direct indication of whether flow is moving in each individual line. If flow was observed to be slowing in a particular line, flow to the line was shut off and the line moved to another injection location. Additionally, if the injection skid was shut off or injection is stopped for longer than an hour, the injection lines were cleared out with clean water and contained in a drum.

During the grout mixing and injection processes described above, procedures were employed to control the process and collect data. During field work, measurements were recorded on a routine specified basis to characterize the process and to facilitate determining design parameters for implementation of Phase 2 and full-scale design. In addition, specific process variables were measured to identify possible system malfunctions or undesirable conditions. These variables include: flow rates, volumes, and injection pressures.

7.4 INJECTION POINTS

Standard permeation grouting practice is not to use a single long injection screen for injection grout. To ensure a good vertical distribution of grout, multiple nested injection points were used in the demonstration based on standard direct push and in-situ remediation technology. The vertical barrier was constructed by injecting the reactive grout mix as a liquid into multi-level injection wells. Figure 10 shows the injection well design. To ensure good vertical placement of the grout, four injection intervals will be used, each served by a 0.5-in diameter PVC injection well or injection tubing. The conceptual figure below shows a well with a 20-ft thick injection zone. Figure 11 shows the plan view of the multi-level injection well.

The injection well system was designed to allow for repeated rapid placement without the need for individual geologic logs at each injection point. Because of the heterogeneous nature of site geology, it was anticipated some of the injection points will likely contact clay and will likely not accept any grout. As these units already have a low permeability, this will not compromise the performance of the barrier. The goal was inject grout in the mobile porosity, primarily the sands and more permeable silts that intersect the flux reduction barrier.

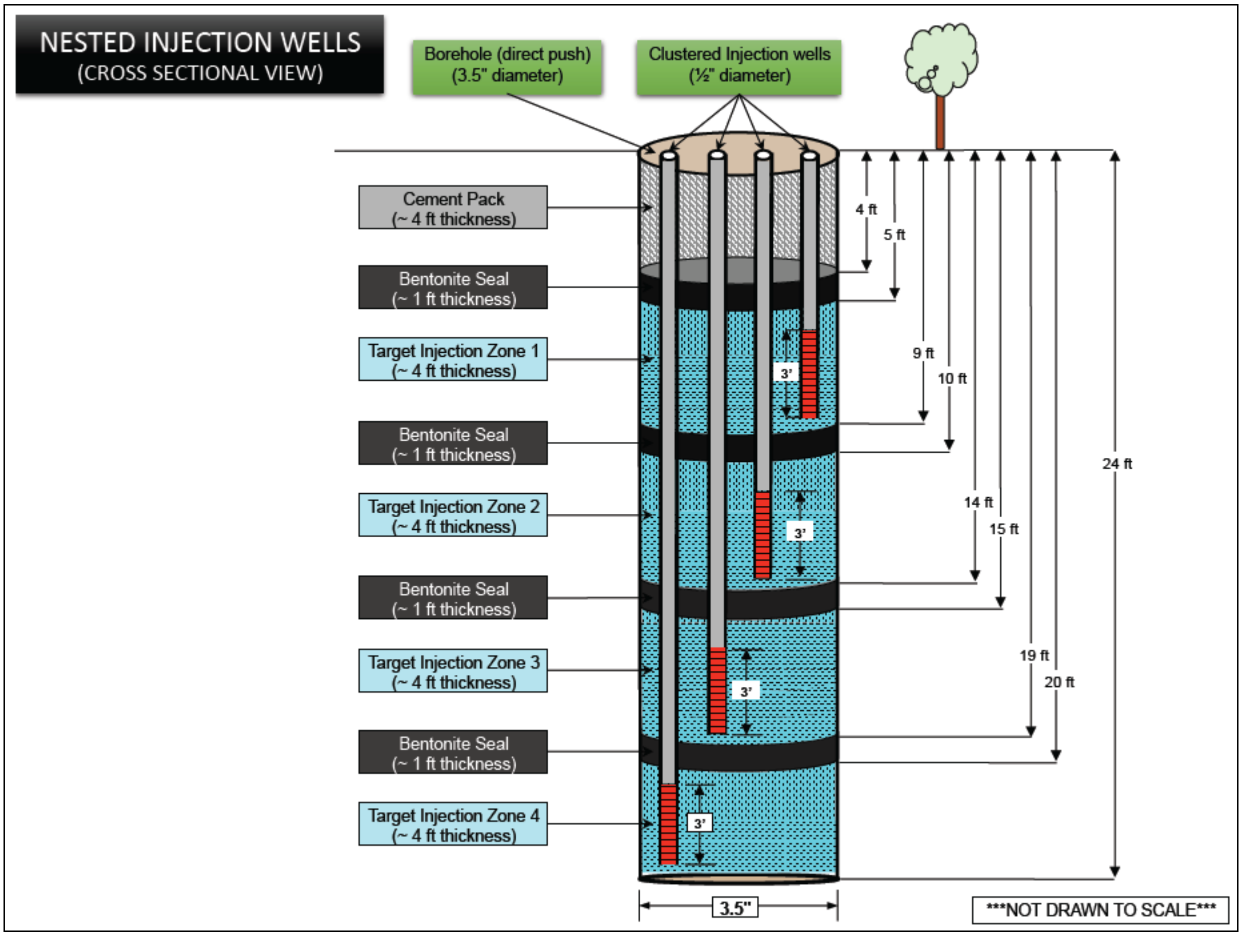

Figure 10. Conceptual Diagram of Direct Push Multi-Level Injection Wells With Four Separate Injection Zones

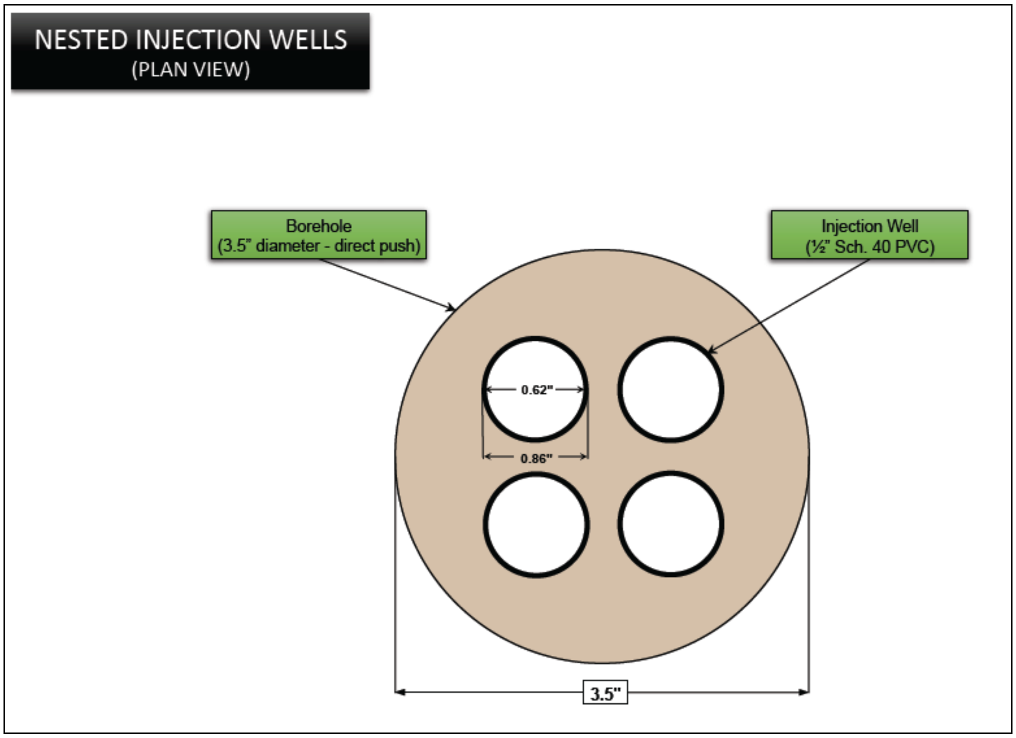

Figure 11. Plan View of Multi-Level Injection Well Design

7.5 PERFORMANCE MONITORING

The reduction in groundwater flow can be measured by two general techniques:

1. **Change in Hydraulic Gradient:** 1) Estimating the groundwater Darcy velocity in the treatment zone before the barrier is installed by measuring the hydraulic gradient and measuring the hydraulic conductivity of the transmissive units within the barrier; 2) then install the barrier; 3) the re-measure the hydraulic gradient. The reduction in flow will be proportional to the reduction in the hydraulic gradient before- and after the barrier is installed.

2. **Use of Passive Flux Meters (PFMs):** Install PFMs (Hatfield et al., 2004; enviroflux.com; ESTCP Project CU-0114) in the treatment zone before and after the barrier is installed.

The benefits from electron acceptor diversion can be assessed using the calculations outlined in Appendix A or by using the BIOBALANCE software tool (Kamath et al., 2008).

8.0 ARE THERE ANY SECONDARY IMPACTS FROM A BARRIER?

Could a flux reduction barrier result in excessive groundwater mounding upstream of the barrier?

Answer: Two lines of evidence indicate that excessive upgradient mounding would not be a problem. First, numerous (likely hundreds) of slurry wall enclosures have been constructed across the country, and it is unknown if any anecdotal reports of excessive mounding in the upgradient direction that have caused any problems. Second, our groundwater modeling indicated that at most only 0.05 ft of upgradient mounding could be expected under typical situations, a level that should not cause any negative impacts. To investigate the mounding, an additional piezometer could be installed upgradient and the change in water level before and after construction of the flux barrier could be measured.

Could a flux reduction barrier reduce the yield of a nearby groundwater pumping well?

Answer: The short answer is a flux barrier would not reduce flow to a groundwater pumping well except in very rare, preventable situations. The conceptual model is similar to a stream: if one places a large stone in the stream, the water will flow around the rock and any water supply withdrawal downgradient or side gradient will not be compromised. Figure 12 below shows how quickly the groundwater streamlines wrap around the barrier, and that normal groundwater flow is restored up to 90 ft downgradient of the barrier.

One theoretical case where a vertical barrier could reduce the yield of a nearby groundwater pumping well would be in a case of small buried valley aquifer, where the barrier would extend across the entire buried valley. This would cause the groundwater to flow in some other direction and potentially reduce well yield. This situation would require a combination of an extremely large barrier in a relatively rare hydrogeologic setting, and be easily recognizable beforehand, so in practice well yields would not be affected by the construction of a barrier.

Will there be more potential for vapor intrusion if the technology is implemented under an active building?

Answer: First, the process as envisioned will not increase the depth to the water significantly. The barriers are not designed to be completely impermeable, and some flow through the barrier is expected. The conceptual model is that groundwater flow alone will not cause the potentiometric surface to increase over the highest groundwater elevation in the vicinity of the barrier (i.e., within a short distance upgradient of the barrier) (Figure 12):

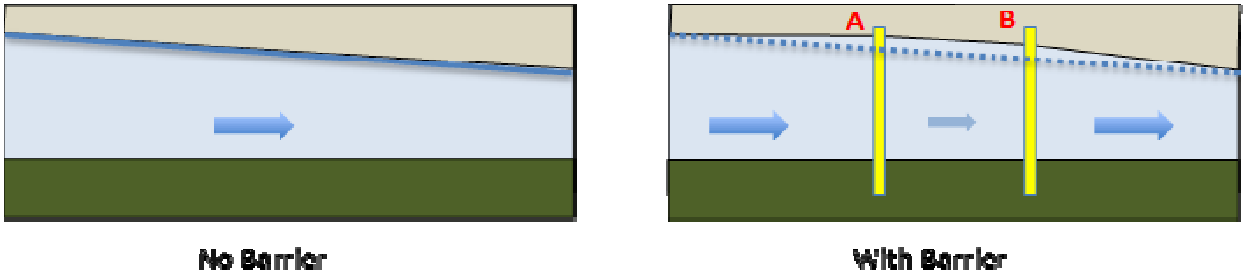

Figure 12. Increase in Groundwater Level Due to Barrier with Conventional Barrier with Some Leakage through the Barrier

<u>Qualitative Assessment</u>

The increase with groundwater elevation at **Point A** is the groundwater elevation a short distance upstream. As demonstrated in the MODFLOW modeling below, this distance upgradient is fairly short, tens or maybe hundreds of ft, but not miles. When this is applied to typical hydraulic gradients in shallow groundwater plumes (1 ft per hundred ft or less) the increase in water level at **Point A** above is limited.

Recharge into the containment zone will result in higher water levels inside the barrier, with the highest elevation increase at **Point B**. However, the experience is that at most contaminated source zones groundwater recharge is a relatively small percentage of the water balance at any site. The reason for this is the amount of recharge upgradient of the source zone that is carried by the groundwater flow in the aquifer is usually much greater than the recharge through the source area alone. A barrier will reduce the natural flow by 90 to 99%, but at many sites the remaining flow will still be greater than the recharge. The water level within the barrier will find the equilibrium level so that the inflow matches the outflow. The conceptual model suggests this will be a relatively small increase in groundwater elevation.

Are there ways to reduce any potential water level increase due to the barrier?

Answer: Two types of engineered factors could be applied to the flux reduction barrier concept to reduce the potential for high groundwater levels that could exacerbate vapor intrusion problems under active buildings.

First, the flux reduction barriers can be constructed with engineered "**spillways**" that would relieve any groundwater mounding within the barrier due to high recharge sites or extreme recharge events (hurricanes), broken water lines, etc. A conceptual picture of the spill way concept is shown below, where the downgradient portion of the barrier is completed at the highest elevation desired by the building and facilities personnel at the site (**Point C** on the Figure 13 below). In this graphic, most of the groundwater leaving the spillway when it is use would be clean water, as any recharge would have a limited ability to mix with deeper contaminants caused by DNAPL. Therefore, the recharge water would not contribute to increased mass discharge from the barrier.

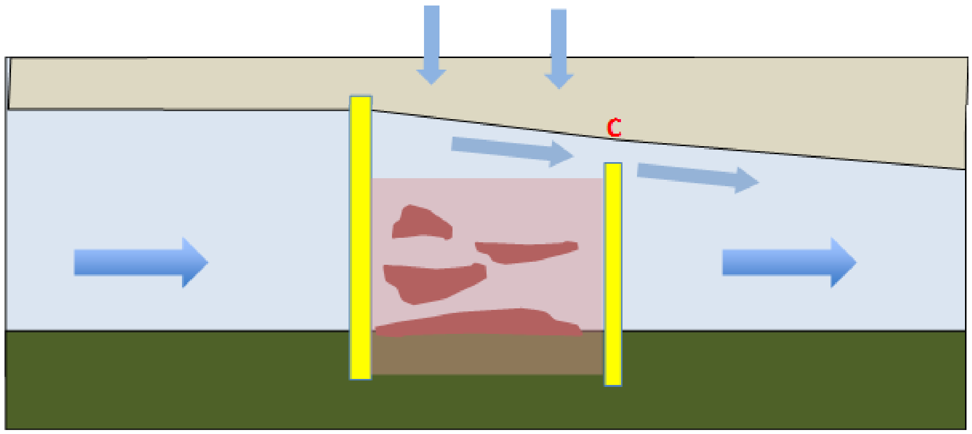

Figure 13. Release of Infiltration Water over Downgradient Edge of Barrier.

As a second engineered factor, any runoff from the building roof and associated parking lots could be **redirected** to areas where this runoff would not be converted to infiltration. Standard stormwater conveyance practices, such as redirecting building downspouts, lining grass swales, and other methods could reduce recharge into the flux reduction barrier. The Final Report will provide guidelines to potential implementers of this technology and describe how simple calculations and groundwater flow modeling can be used to determine if these improvements should be performed a priori.

In the unusual case where elevated groundwater conditions are observed after construction, these stormwater conveyance practices can be implemented as a mitigation measure to reduce the influx of recharge into the barrier.

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9.0 HOW MUCH DOES A BARRIER COST?

9.1 ESTIMATED COSTS AT A HYPOTHETICAL SITE

Applicable costs associated with the field program element of the demonstration study have been employed to develop costs for full-scale implementation of a flux reduction barrier for remediation of affected groundwater. Based on a typical application of the technology at a hypothetical site, full-scale implementation costs have been estimated. Some tasks and associated costs incurred during the field demonstration would not be applicable for a full-scale implementation of the technology; therefore, costs for these items have not been included for the full-scale remediation. A summary of the cost considerations is provided below; see the Cost and Performance Report for more detail (Kulkarni et al, 2017b).

Costs of a full-scale installation of a flux reduction barrier were estimated using the following assumptions regarding the site:

- Treatment Area: A rectangular are with the dimensions of 218 ft by 200 ft, corresponding to an area of 43,600 ft^2 (i.e., slightly more than one acre) and a total perimeter of length of 836 ft.
- Injection Point Spacing: 4 ft along perimeter
- Depth of Treatment Zone: From 5 ft bgs to 35 ft bgs, corresponding to barrier thickness of 30 ft
- Porosity of Treatment Zone: 30%

Costs were also dependent on the following considerations:

- Grout: Standard NaSi solution with DBE hardener having the following composition: 10% NaSi, 5% DBE, 85% water (by volume)
- Cost for Grout Components: Cost of NaSi, DBE, water and water tank rental projected based on incurred field demonstration costs.
- Time for Implementation: Drilling and injection time estimated based on experience gained during field demonstration.
- Decommissioning: Decommissioning costs estimated to be identical to the incurred field demonstration costs.
- Additional Work: No performance assessment tests to be conducted.

Table 3 below summarizes the results of the projected costs at the hypothetical site. As such, for a 1-acre site with a total barrier thickness of 30 ft, the total cost of the technology implementation is approximately $996K. Subsequently, the cost per cubic yard is $21/cubic yard ($yd^3$).

Table 3. Estimated Costs of Implementation at a Hypothetical One-Acre Site

Cost Category	Subcategory	Description	Estimated Cost	Notes
PROJECT PLANNING AND DESIGN	Treatability Study	n/a	--	Not applicable
	Engineering Design and Site Assessment	Labor	$65,000	Estimated
		Grout mix materials and testing	$1,550	Estimated
		Misc. equipment (testing beakers, etc.)	$500	Estimated
FIELD PROGRAM	Injection Skid and Materials	Injection Skid + Start-Up Support (Subcontractor)	$50,000	See Table 7.3 for parameters and assumptions
		Injection Grout Materials, transportation, and Water + Tank Rental (Sodium silicate tote, dibasic ester drum)	$421,900	See Table 7.3 for parameters and assumptions
	Installation and Strat-Up	Drilling Subcontractors (including utility clearance)	$337,000	See Table 7.3 for parameters and assumptions
		Other Equipment Rental (Generator, forklift, car rental)	$9,700	See Table 7.3 for parameters and assumptions
		Labor + Other Expenses (meals, lodging, travel)	$102,000	See Table 7.3 for parameters and assumptions
	Performance Assessment	N/A	--	
DECOMISSIONING	Decomissioning	Waste Disposal of remaining materials, including lab analysis; labor; transportation of skid.	$8,600	See Table 7.3 for parameters and assumptions
		Total for 1 Acre Site ($)	***$996,250***	
		Treatment Volume (yd^3)	***48,444***	
		Cost per Cubic Yard ($/yd^3)	***$20.6***	

9.2 COMPARISON OF FLUX REDUCTION BARRIERS WITH OTHER TECHNOLOGIES

The typical cost of installing a flux reduction barrier for remediation of groundwater affected with chlorinated organics has been compared to the typical cost of implementing Enhanced In Situ Bioremediation (EISB), In Situ Chemical Oxidation (ISCO), Thermal Treatment, and Pump and Treat projects at a Case 1 Study Site (Table 4), as described in Harkness and Konzuk's Chapter 16 in Kueper et al. (2014).

Table 4. Description of Case Study Site

Parameter	Case Study Site
Area	1,500 m^2 (16,145 ft^2; 0.11 acre)
Depth to Groundwater	1.5 meters (m) (4.9 ft)
Depth to Aquitard	4.5 m (14.8 ft)
Saturated Thickness	3.0 m (9.8 ft)
Porosity	0.3
Groundwater velocity	32 m/yr (105 ft/yr)
Barrier Thickness	3 m (9.8 ft)

Additionally, in order to provide an equal comparison, costs for a Flux Reduction Barrier was estimated for the parameters outlined in the Case Study Site (Table 7.5). Also, a total monitoring time period of source area monitoring wells for 10 years is assumed for all technologies. For Flux Reduction Barriers, assessment of mass flux is included in monitoring, in addition to groundwater analyses.

As seen in Table 5, the total project cost for these technologies ranges from $1,200K to $3,960K, as compared to that of $640K for Flux Reduction Barriers. As such, Flux Reduction Barriers are the more cost-effective technology alternative.

Table 5. Cost Comparison of Flux Reduction Barriers with Other Remedial Options

Cost Component	EISB	ISCO	Thermal	Pump and Treat	Flux Reduction Barriers
Design	144	134	248	254	67
Capital	592	705	2080	465	282
O&M	184	990	0	2967	0
Monitoring	277	277	277	277	291
Total ($K)	**1,200**	**2,100**	**2,600**	**3,960**	**640**
Total ($/yd3)	**663**	**1,170**	**1,440**	**2,200**	**355**

*Note: monitoring costs for EISB, ISCO, Thermal, and Pump and Treat assumed to be all for 10 years for comparison purposes. Keuper et al., 2014 listed varying monitoring time periods for these technologies.

9.3 COST DRIVERS

The cost of implementing flux reduction barriers is driven by the following factors: (i) treatment depth, (ii) site geology and injection point spacing. These factors influence the total volume of injection material required, as well as the drilling time for injection point installation.

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10.0 WHAT HAPPENED IN THE FIELD DEMONSTRATION?

Key results from this ESTCP project are summarized below:

- Two grout mixtures were selected based on gel tests and a treatability study by Solutions-IES:
  - A *Silica Gel Grout:* 10 vol-% of NaSi, 5 vol-% of DBE hardener, and 85 vol-% of water. This formulation had a gel time of approximately 4 hours and had an estimated viscosity of 3-4 cP.
  - *Solutions-IES Novel Silica Gel/Veg-Oil Grout:* 5-percentage by weight (wt-%) of EVO, 10 wt-% of NaSi, 1.8 wt-% of DBE, and 83 wt-% of water. This formulation provided a 3-4 orders of magnitude reduction in lab permeability tests, and a gel time of 18 hours.

- A Small-Scale Demonstration was performed, but resulted in a 64% reduction in groundwater flow (Figure 14). The reason for the lower-than-expected performance was likely the low hydraulic conductivity ($7x10^{-5}$ cm/sec) in the test area that had two effects: (1) it was on the low range of recommended application range for silica gels, making it difficult to emplace the grout; (2) it made it difficult to accurately measure barrier performance. This 64% reduction was below the 90% reduction flow reduction goal established in the ESTCP Demonstration Plan.

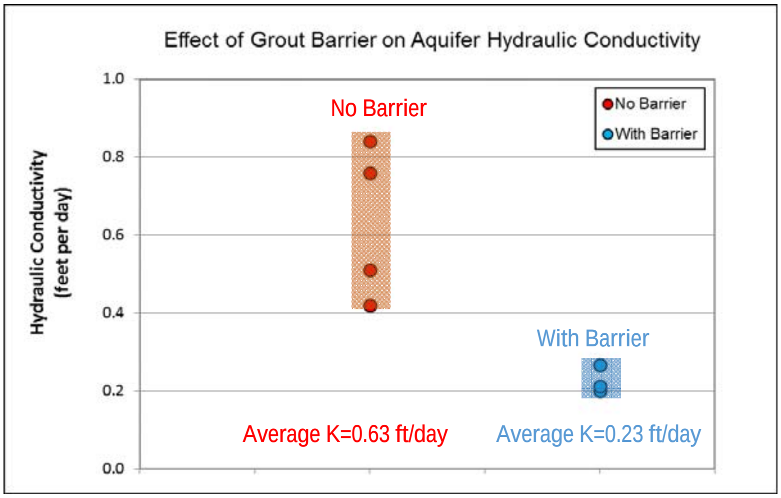

Figure 14. Results of Small-Scale Demonstration

- The planned Large Scale Demonstration was not performed due to: (1) the Small-Scale demonstration did not achieve the 90% flow reduction performance goal; and (2) the low permeability of the planned test area was at the low end of the scale for successful application of permeation grouting. However, based on standard geotechnical practice, 90% groundwater flow reduction with silica gel permeation grouting is likely achievable at sites with the main transmissive units having hydraulic conductivity closer to the optimal range (from $5x10^{-4}$–10^{-2} cm/sec).
- Other grouts are available for conditions outside the optimal range for silica gel: cement grouts for units above $1x10^{-1}$ cm/sec, and acrylate grouts for lower permeability units. Note that these grouts are more expensive than silica gel (particularly the acrylate grouts).
- Based on field experience of the Small-Scale Demonstration, the process is moderately complex to implement in the field but with no major problems.
- The Solutions novel silica gel/vegetable oil grout behaved similarly as the conventional silica gel grout. Because the Large Scale Demonstration was not performed the biodegradation function of the Solutions grout could not be assessed.

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APPENDIX A
TCE MASS REMOVED BY ELECTRON ACCEPTOR DIVERSION

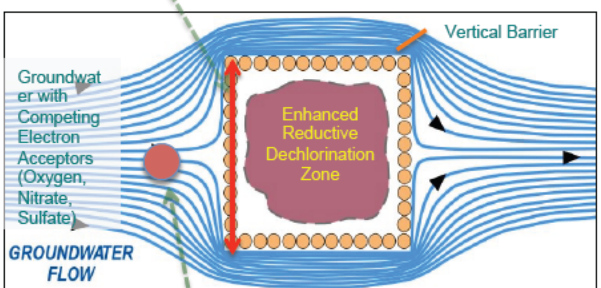
ESTCP Barriers Project

User Input
Calculated
Literat. Value

CALCULATE REDUCTION IN FLOW AT HYPOTHETICAL SITE

			Notes
b = saturated aquifer thickness	6.1	m	Thickness of transmissive zone; from boring logs
i = regional hydraulic gradient	1.0E-02	m/m	From potentiometric surface maps
K = hydraulic conductivity	0.0200	cm/sec	From slug test, pump test, estimates based on material
Width of barrier / treatment zone perpend. to flow	137	m	From plume/source zone maps
Groundwater Darcy Velocity (K*i)	6.3	m/yr	Calculated; can overwrite if desired. Do not use seepage vel
Volumetric Groundwater Flowrate	5,246,525	Liters/year	Calculated; can overwrite formula if desired
% Reduction in Flowrate After Barrier Construction	90%	%	Performance of barrier; 90% is typical for pemeation groutir
Volume Groundwater Diverted	4,721,872	Liters/year	Calculated; can overwrite formula if desired

Plan View of Barrier



Get these data from background monitoring well(s) upgradient of the source

CALCULATE INCREASE IN BIODEGRADATION DUE TO ELECTRON ACCEPTOR DIVERSION

lbs TCE degraded to ethene per lb of H2:	22
Assumed Efficiency (% of hydrogen going to dechlorination)**:	50%

Competing Electron Acceptors in Upgradient Groudnwater	Concentration in Groundwater Entering Source Zone (mg/L)	Difference in Electron Acceptor Mass Discharge (kg/year)	H2 Equiv. Per kg Analyte*** (kg/yr)	H2 Equivalents (kg/yr)	Assimilated Capacity for TCE (kg/yr)
DO	8	38	*8.0*	4.7	52
Nitrate	6	28	*12*	2.3	25
Sulfate	50	236	*12*	20	216
Total				Total:	**293** **kilograms/year**

This is the amount of extra CVOC biodegradation that could occur if a barrier is installed and competing electron acceptors are diverted away from the source zone.

Add this value to reduction in CVOC mass discharge due to the barrier to get the toal benefit from a barrier project.

* Newell and Aziz (2004) (Median from Table 1)

** Newell and Aziz (2004) assumed 100% effiency to demonstrate potential of diversion
This parameter is difficult to estimate, but After a few years, the hydrogen will go to either methanogenesis or dechlorination. 50% is a good planning level value.

*** BIOBALANCE Tool